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NITROGEN IN THE SUBSURFACE ENVIRONMENT

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SECTION I

CONCLUSIONS

A survey of the literature which is currently available concerning nitrogen and its compounds in relation to the subsurface environment leads to the following conclusions:

1. Increased quantities of various forms of nitrogen are being released to the soil systems and higher concentrations of nitrogenous compounds are consequently making their way into subsoil regions.

2. Knowledge of the behavior and fate of nitrogenous chemical species in the subsurface environment is needed by those concerned with the prevention and control of ground-water pollution.

3. Any nitrogen compounds can be leached if the proper conditions are satisfied. The rate and amount of nitrogen leached from soil is dependent on soil characteristics, climate, biological characteristics, use of the soil system, and the amount and form of nitrogen present.

4. Compounds of nitrogen can move through porespaces of soil as gases or as solutes in aqueous solution. The distance, direction, and amount of nitrogen transported varies with time as well as chemical, biological, and physical properties of the soil. Each soil profile is unique due to its geology, topography, climate, and the vegetation that exists at each site.

5. Nitrification and denitrification reactions occur in the soil systems and these reactions are dependent on factors such as soil texture, moisture, temperature, pH, etc.

6. Nitrogen contamination of ground-water supplies can be attributed to a number of sources such as agricultural fertilizers, animal wastes, domestic waste, and natural

sources. Each case of contamination must be examined individually in order to determine the source of pollution.

7. A potential health hazard does exist from the ingestion of nitrate in water supplies. The most apparent danger is to those infants less than six months of age, but the nitrite ion could cause methemoglobinemia in adults if it is prasent in sufficient concentrations. The effects of long term ingestion of low concentrations of nitrate is not known.

SECTION II

RECOMMENDATIONS

It is recommended that studies be initiated which would focus attention on the movement and fate of nitrogen in the subsurface environment. The various possible reactions of nitrogen compounds in the subsurface environment and the factors affecting these reactions should be stressed. This could give valuable information concerning the role that microbial reactions in the subsurface environment play in relation to ground-water contamination. As a result of these studies, those individuals concerned with the protection of ground-water supplies could direct proper control measures.

It is also recommended that careful attention and planning be given to the proper agricultural practices involving the use of fertilizers, irrigation practices, and livestock handling operations. All of these have been cited as potential sources of ground-water contamination and careful planning could possibly prevent the further contamination of underground water supplies.

Since it is realized that nitrogen can be leached after it is added to the soil, care should be exercised in the way man disposes of the sewage and solid waste which he generates. Proper means of disposing of domestic waste and solid waste should be emphasized and research concerning better means of disposing of these types of waste should be stressed.

SECTION III

INTRODUCTION

Nitrogen is a unique element in the ecosphere, comprising approximately 80 per cent of the earth's atmosphere. Some oxidized forms of nitrogen are essential for life; however, nitrogen in the elemental form is relatively inert and is not a suitable source of the element for most living forms.[1] The demand for food is continually increasing throughout the world and the oxidized forms of nitrogen can be a limiting factor to the amount of food that can be produced in a specific locality. Some concentrations of the oxides of nitrogen are added to the soil through natural processes such as lightning, microbiological oxidation of ammonia known as nitrification, and by man's activities in urban and rural living.[2] But to meet the increasing demand for food by an expanding population, the oxidized forms of nitrogen have been introduced to soil systems by new technology rather than the slow processes of nitrification or symbiotic nitrogen fixation.

Until recently, the main reason for investigations concerning the oxidized forms of nitrogen in soil systems below the rooting depth of plants was to evaluate the loss of nitrate to the crop and to estimate the loss of production. In recent years, attention has been focused on these oxidized forms of nitrogen as potential pollutant sources of both ground water and surface water.

Ground water is that water in the saturated zone beneath the earth's surface, and although less easily polluted than surface waters, potential for pollution of ground water is increasing. In the United States there are approximately 13 million septic tanks and numerous lagoons or leaching ponds employed for disposal of domestic, industrial, and agricultural wastes. Also there are soil treatment systems, landfill operations, and agricultural operations, all of which are considered to be potential sources of nitrogen pollution of ground water.[3] In 1970, the total withdrawal of fresh ground water in the nation was 68 billion gallons per day, accounting for approximately 20 per cent of the total quantity of water being used for all purposes in the United States.[3,4] With the expected growth in water demands, it is almost certain that ground-water resources will be increasingly used to satisfy man's future needs. In order to meet these future needs, the ground-water resource must be maintained in a form which will not produce adverse effects on humans and animals.

The oxidized forms of nitrogen are soluble in water, and the nitrate and nitrite ions are negatively charged. Therefore, the potential for these forms of nitrogen to move between negatively charged soil micelles in the soil system and make their way toward ground-water zones is great once these ions are in the soil system.[5,6,7]

Health hazards can exist for humans (especially infants) and domestic animals if some forms of nitrogen are in water supplies in significant concentrations. The most apparent danger to humans concerns nitrate ingestion in those infants less than six months of age.[8]

Methemoglobinemia is caused by bacterial conversion of nitrate to nitrite, which chemically combines with the hemoglobin of the blood to form methemoglobin. The bacteria necessary for the conversion of nitrate to nitrite are more likely to exist in infants because the pH of an infant's stomach is more suitable for the growth of nitrate reducing bacteria. Once the nitrite has combined with the hemoglobin to form methemoglobin, the oxygen carrying capacity of the blood is reduced and methemoglobinemia, characterized by asphyxia and possible death, may result.[9,10] Approximately 2000 cases have been reported in North America and Europe with a fatality rate of 7 to 8 percent.[8] Since the condition (methemoglobinemia) is not a reportable disease, it is conceivable that this number is only a small percentage of the actual number of cases.

Although most of the public health concern in relation to nitrogen and ground water has been centered around the nitrate form, it should be emphasized that the nitrite ion is much more aggressive than the nitrate ion.[11] If the nitrite form is present in water supplies, methemoglobinemia can be expected to result in the adult population. Also, it should be noted that nitrite is present in some shallow wells, probably from percolation through the soil system under waste disposal systems.[11,12] There is also some concern about the concentration of nitrite which might be formed by biochemical processes in the subsurface environment, thus making its way into the ground-water system.

The long term effects of exposure to low concentrations of nitrate and nitrite are unknown. Authorities do not agree on the safe limits of nitrate or nitrite in water supplies, but as a safeguard for people in metropolitan areas, the United States Public Health Service has set a safety limit of 45 mg/l nitrate or 10 mg/l nitrate as nitrogen, for municipal water supplies.[2,13] This is also the concentration of nitrate proposed for the National Drinking Water Standards by the Environmental Protection Agency. Some authorities feel that the tolerance for infants is even lower than this value. Although no limit has been set specifically for rural domestic supplies, the potential dangers of nitrate concentrations greater than 45 mg/l should be recognized. Domestic animals, including poultry, have also been shown to be sensitive to nitrates and nitrites.[12,14] These anions have been shown to inhibit iodine and vitamin A metabolism in research animals.[15]

Because of the importance to agriculture, the movement and reactions of nitrogen in the topmost layers of the earth's crust, considered by soil scientists as true soil, have received much attention. The fate of nitrogenous materials in those regions of the earth's crust underlying the soil zone has, however, been given relatively little attention. Since increased quantities of various forms of nitrogen are being released to the soil and higher concentrations of nitrogenous compounds are consequently making their way into subsoil regions, knowledge of the behavior and fate of these substances in the subsurface environment is needed by those concerned with the prevention and control of ground-water pollution. This paper presents information concerning the nature and origin of nitrogenous substances polluting ground water, the probable movement and reactions of nitrogenous compounds in the subsurface environment, and specific cases of ground-water pollution by nitrogen-containing compounds.

SECTION IV

FORMS AND SOURCES OF NITROGEN IN GROUND WATER

Nitrogen is a diatomic element existing in the gaseous state and is the most predominant species in the atmosphere. This element is capable of exhibiting a number of oxidation states and combining with a number of other elements to form organic and inorganic compounds. Nitrogen is an essential nutrient for plants and animals and is found in all protein materials. Nitrogen exists in a number of other naturally and synthetically produced organic and inorganic compounds. The inorganic forms of nitrogen which are common in nature are the nitrate, nitrite, and ammonium ions.[16] Nitrate and nitrite are anionic species which are often found in combination with sodium, potassium, calcium, magnesium, and other monovalent and divalent metallic ions. Ammonia readily forms the ammonium cation which is commonly found in nature with a number of the metallic cations.

The compounds and ionic species of nitrogen have been implicated as pollutant materials of surface water for a number of years, but in recent times more attention has been directed toward nitrogen and its role in the contamination of ground-water supplies. Organic nitrogen has not received as much attention as the ionic form of nitrogen, but the presence of organic nitrogen in some underground water supplies is to be expected. In locales with swamps or marshes having high water tables, the potential for leaching organic nitrogen could be expected. Some of these organic compounds could be highly mobile and easily transported through the soil by percolation. The presence of organic nitrogen in some water supplies can be expected in close proximity to landfills, livestock operations, and sewage treatment facilities.

The presence of the ammonium ion in ground-water supplies has not received as much attention as some other inorganic forms, but investigations have confirmed its presence in some locations. One investigator in Colorado confirmed the presence of the ammonium ion in conjunction with organic carbon and noted that some samples of ground water even exhibited offensive odors.[17] An ammonia molecule can readily combine with an available proton to form an ammonium ion which is positively charged. It is this positive charge which causes most of the ammonium ions to be held in the soil profile by the negatively charged soil micelles.[18] In general, clay soils hold ammonium ions more efficiently than sandy soils, soils of low pH more efficiently than those of high

pH, and soils with high organic contents are less efficient than mineral soils with similar cation-exchange capacities. The ammonium ion can be leached, however, through the soil profile if the cation exchange capacity of the soil is satisfied.[18]

Most investigations concerning nitrogen and ground water have been directed toward the inorganic anionic species, especially the nitrate ion. Nitrate and nitrite anions are negatively charged and the movement of these species through the soil profile is accelerated because of the anionic state of most of the soil mineral fractions. Little inhibition to movement exists for these ions when in soil solution.[19] The determinants of movement in the profile are the amount of water infiltrated into the soil, the soil moisture content at the start of the precipitation event, the porosity of the soil, and its permeability.[5] The nitrate species is more stable than the nitrite and, therefore, is more commonly encountered in soil and water systems, although investigations have confirmed the presence of the nitrite ion i a number of well water supplies.[11,12] Crabtree's investigation in Wisconsin showed that there was no clearly defined relationship between the depth of the well and high nitrate concentration for the area, but a trend did exist between increasing nitrite concentration and well depth. The highest incidence of nitrite occurred most commonly in shallow and dug wells immediately after heavy precipitation.[12]

Nitrogen contamination of ground water can be attributed to a number of sources. The most widely recognized sources are fertilizers, animal wastes, and domestic wastes. However, investigations of nitrogen sources which can account for contamination of ground-water supplies indicate that much of the contamination can be attributed to natural sources--that is, those not directly related to man's activities.[11] Some microorganisms are capable of taking nitrogen directly from the air and converting it into usable forms. There are estimates that some 44 million metric tons leave the atmosphere by this procedure annually.[20] Some of the nitrogen from this process can possibly percolate downward to ground water. The atmosphere is considered to contribute from 0.9 to 2.7 kilograms (2 to 6 pounds) of nitrogen to an acre of land over the period of a year.[12,21,22,23,24] The degradation of vegetation--especially old stands of alfalfa--can also contribute much nitrogen to the soil.[25] Soils contain other sources of organic matter which can be broken down and converted to usable forms.[26] The inorganic forms of nitrogen placed in the soil in this manner are capable of being leached from the upper soils to underground water supplies.

Some natural soil deposits such as organic rich shale and some deposits of limestone contain considerable amounts of nitrate which can be leached.[12,27,28] Investigations in Missouri indicate that the potential source of nitrogen contamination of some streams is probably the bat guano mounds in caves in close proximity to those streams.[28,29,30]

Rainfall and dust are two other natural sources of nitrogen which should not be overlooked. Much nitrogen is added to the soil by both of these methods.[31,32,33,34,35] Rainfall, dew, and snow can contain

various forms of nitrogen, and Walker indicates that the nitrogen additions by this method may be as much as 7 kilograms (15 pounds) of nitrogen per acre per year in some localities.[36,37,38] Very little information is available concerning the amount of nitrogen which may reach the soil systems from the settling of dust, but one investigator feels that as much as 4.5 kilograms (10 pounds) of nitrogen per acre per year is possible.[39] Much of this nitrogen is being recycled from the soil or barnyard and some can be attributed to salts formed in the atmosphere.[36,40,41,42,43]

Animal waste materials contain nitrogenous compounds which are converted to ammonia during the decomposition process. The ammonia can then be converted to nitrite and nitrate ions. This process is characteristic of the waste from all animals, but man's handling of domestic animals has created a serious threat to water supplies.[43,44,45] The practice of confining large numbers of animals together in restricted areas creates high concentrations of pollutant materials in a locale.[37,46]

The present methods of handling the vast accumulation of animal waste, usually piling, spreading, or lagoon treatment, does not prevent the nitrogen forms from being a potential pollutant source.[47,48,49] Farm manure contains about 4.5 kilograms (10 pounds) of nitrogen per ton of dry matter and poultry waste is even higher.[7] Estimates concerning the amount of nitrogen waste per animal vary but some authorities attribute about 43 kilograms (95 pounds) of nitrogen per year for each animal in a beef feedlot operation.[16] Investigations reveal that the nitrate contamination of water supplies is common around dairy operations, barnyards, and feedlots, with feedlots presenting the most serious problem in many parts of the country.[50,51] One investigator in Missouri found over 920 kilograms (2022 pounds) of nitrate nitrogen per acre at a depth of 4.3 meters under a feedlot operation.[25] Similar accumulations have been reported in Colorado under conditions of lower precipitation.[52]

Another potential source of nitrogen contamination not often recognized involves the handling of silage. The leachate from silage is rich in organics and sometimes tremendously high in nitrogen; this leachate has been shown by some investigators to be a problem in the area of water contamination.[38]

An agricultural practice which has received a great deal of attention as a potential source of nitrogen contamination is the use of commercial fertilizers. Fertilizers account for more than 30 per cent of the food produced in the United States at the present time.[10] In 1970 the United States consumption of commercial fertilizers was approximately 36,000,000 short tons, and it is estimated that 70,000,000 short tons will be used annually by 1980.[53] Nitrogen fertilizers constitute the largest share of the fertilizer market.[38,54,55]

This topic has been and will continue to be a controversial issue. Investigations of nitrogen levels in central Illinois indicate a correlation between the usage of nitrogen fertilizers and levels of

nitrate found in the rivers of the area.[56] Walker's work in Illinois also reveals the close correlation that occurs between fertilizer usage in Illinois and levels of nitrate in ground water.[57,58] Dependency of the ground-water nitrate levels on the fertilizer management practices for cropping systems in the California area are indicated.[59,60,61,62]

The effects of fertilization on the nitrogen content of surface runoff and ground water show variations from locale to locale. The nitrate content of the waters of the upper Rio Grande did not show a significant increase in nitrate concentrations over a thirty-year period even though the rate of application of the nitrogen fertilizers increased from a low level to a high level over the period.[63] However, an investigation by Stewart in Colorado revealed that nitrate is moving through the soil and into the ground-water supply under both feedlots and irrigated fields, excluding alfalfa.[52] This study showed that larger amounts of nitrate are present under feedlots than irrigated lands, but that irrigated lands are contributing more nitrate to the ground water since the ratio of irrigated land to that in feedlot for the study area is 200 to 1. In Missouri, the only waters considered contaminated by nitrogen fertilizers were located under light sandy alluvial soils along the Mississippi and Missouri Rivers.[29] The varied results of studies of fertilizer effects on the nitrogen levels of ground and surface waters emanating from crop production areas imply that each area and cropping system utilized will have to be examined for the pollution effects resulting from the use of nitrogen fertilizers.[64,65]

Irrigation practices in conjunction with fertilizer applications have received some attention, and the increased amount of nitrogen in ground-water supplies in some regions of California has been attributed to the liberal uses of fertilizer in conjunction with irrigation.[59,61,66,67] It appears that heavy application on highly permeable soils has contributed significant amounts of nitrogen to underground water supplies.[60,62,68] Since a number of factors, such as improper application practices, soil conditions, etc., are important, fertilizers should be recognized as a potential source of contamination of ground-water supplies and in some localities even a major potential source of nitrogen contamination.[56,65,69,70] Improper handling of fertilizers before they reach crop lands should also be considered a potential source of contamination due to accidental spills and leaching from storage sites.[71]

Runoff from land has been recognized as a source of nitrogen pollution, but it should be stressed that this source should include runoff from all land, not just that land under cultivation.[36,44,72,73] Until very recent times, little attention had been devoted to runoff from urban land, but recent investigations cite this as a potential pollution source. Water of this type is known to contain nitrogen from lawn fertilizers, dust fall, leaves, waste materials from domestic pets, household wastes, etc.[54] Investigations by Keeney show that the nitrogen content of urban runoff is sometimes higher than the nitrogen content of sewage.[36]

The disposal of human wastes has been recognized as a potential source of contamination of ground-water supplies, and none of the commonly used methods of treatment, in rural or urban areas, can eliminate nitrogen as a potential source of pollution. The average amount of nitrogen released by each individual is considered to be about 5.4 kilograms (11.9 pounds) per year.[16] If only a small portion of the nitrogen from human wastes makes its way to the ground water, the impact on these supplies could be serious.

The nitrogen contamination of a number of wells in urban and rural areas has been attributed to septic tanks. The septic tank system is the predominant method of sewage disposal in rural areas and is still widely used in many urban areas as well. It is estimated that 25 percent of the population of the United States use septic tanks or cesspools for the treatment of household wastes. In Nassau County, Long Island, New York, the daily discharge into septic tank systems is estimated to be 300 million liters (79 million gallons).[16,75] The waste materials from humans contain a number of nitrogenous materials which are largely converted to ammonia in septic tank treatment systems. Much of the ammonia is removed by soil fixing and adsorption, but under the right conditions, the ammonia can be converted to nitrate and nitrite, which can readily be leached to ground water. In addition to the effluent from the septic tanks, the sludge removed from these systems is high in nitrogen and can be a problem if improper disposal occurs.[16]

In addition to septic tanks, much of the human wastes in urban and rural areas is treated by cesspools, privys, and lagoon systems. With all of these methods of disposal, there is a potential for the nitrogen in the treated effluents to leach to ground-water supplies and the contamination problem may persist for years after such systems are discontinued.[76]

Conventional treatment systems are not to be eliminated as potential sources of nitrogen pollution of ground-water supplies. It is estimated that about 75 percent of the population in the United States is now served by sewer systems. Primary treatment removes approximately 5 percent of the nitrogen from sewage and secondary sewage treatment removes less than one-half.[16,36,74] Therefore, the effluent from such systems contains large amounts of nitrogen, some of which can travel through soil systems to ground-water supplies. Also, that nitrogen removed by sewage treatment is retained in sludge and may be leached into ground water if the sludge is handled by normal land disposal methods.

A recent investigation concerning the contamination of ground-water supplies in the northeastern United States revealed that sewer lines are also a source of contamination. In King County, New York, the nitrate contamination of a water supply was attributed to a broken sewer line.[75] It is a known fact that many of the sewer lines in the United States are old and contain breaks which allow the leaching of pollutants to ground-water supplies. It is difficult to estimate the amount of contamination which occurs from these sources.

Another problem area involving the handling of man's waste is the practice of solid waste disposal. It is estimated that 2.42 kilograms (5.3 pounds) of solid waste are generated per person per day and that about 90 percent of this material is disposed of in landfill sites.[16,75] The nitrogen content of most solid waste material is about 0.5 percent so about 800,000 metric tons of nitrogen is buried in this manner each year in the United States.[16] A leachate is formed in the course of aging of the system, and investigations reveal that this aqueous phase is high in nitrogen.[77] The leachate coming from a landfill may contain high concentrations of nitrogen for several years after the use of the system is discontinued.

Some industrial operations are known to contribute significant amounts of nitrogen to soil systems, creating a potential for leaching to ground-water supplies. Coking processes, petroleum refining, dairy processing, and meat processing are only a few of the activities known to produce liquid waste materials high in nitrogen.[36] Also, some attention has been devoted to those industries producing nitrogen containing compounds such as the fertilizer manufacturing operations.[53] These and many other industries sometimes use surface impoundments for the treatment of materials which cannot be discharged to municipal treatment systems. In a survey conducted in the northeastern states, 57 cases of ground-water contamination from such industrial surface impoundments has been noted.[78] The majority of these 57 cases of contamination included nitrogen as one of the pollutant materials.

The contamination of some ground-water supplies in several sections of the country has been attributed to the draining of wetlands. Marsh or swamp waters may contain high concentrations of nitrogen. When the wetlands are drained, anaerobic activity stops, and some of the nitrogen is oxidized and, therefore, subject to leaching through the soil systems.[36,79]

Wastewaters are sometimes purposely disposed of or recharged to the underground in a number of different ways. These methods of recharge involve discharging the wastewater to deep wells, shallow wells, pits or basins, or irrigation plots. These practices have become more popular in recent years with the increased restrictions on waste discharge to surface waters. There is not a great deal of information available about these methods and their effect on the subsurface environment, but all can serve as potential sources of ground-water contamination.[72]

SECTION V

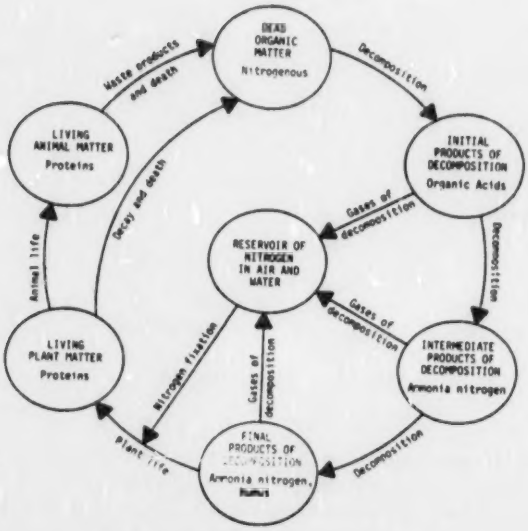
MOVEMENT AND REACTIONS OF NITROGEN IN THE SUBSURFACE ENVIRONMENT

It is obvious that compounds of nitrogen from a number of sources may enter ground-water supplies and that nitrates and nitrites are probably the nitrogenous substances of most significance as pollutants because of their mobility in soil profiles and their health effects. Understanding and controlling the pollution of ground water by nitrogenous substances, however, requires knowledge of the transport of the substances and the reactions which they may undergo in the subsurface environment.

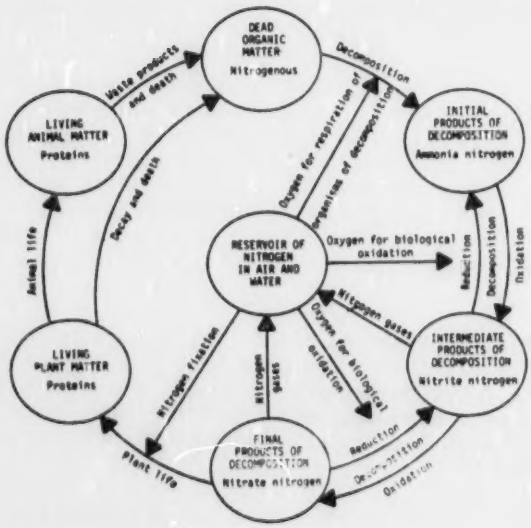
Nitrogen may move through the subsurface zones by several modes which can operate independently or in conjunction. Compounds of nitrogen can move through the soil porespace as gases or as solutes in aqueous solution. Nitrogen fixed in insoluble organic matter or in mineralized form may be transported through the soil profile by organisms (through excretion or mechanical transport) or by suspension of the particles in soil water. The distance, direction and amount of nitrogen transported varies with time and with chemical, biological and physical properties of the soil.

The soil profile at each geographical location is unique in its nitrogen transport capability. This uniqueness is the result of the specific culmination of geology, topography, climate, and vegetation that exist at each site and each parameter can influence the part played by other variables. A mathematical review of the kinetics of transport is provided by Garner.[81]

The transport of nitrogen in the subsurface environment is, of course, a function of the types of nitrogenous compounds present and, hence, dependent on the transformations which these compounds may undergo in this environment. The simplified nitrogen cycle in Figure 1 describes dynamically the transformations of nitrogen compounds as they are known to occur in the surface and shallow subsurface environments. In considering this figure, it should be noted that the term "cycle" does not imply that the nitrogen atoms are moving through the cycle from step to step in an eternal movement. The pathway of nitrogen atoms is



(a) aerobic decomposition



(b) anaerobic decomposition

Figure 1. Nitrogen cycle

not progressive nor continuous, and it is possible for an atom of nitrogen to stay at one place in the cycle.[16]

Microorganisms play an important role in the nitrogen cycle, particularly in the soil environment. Over 90 percent of the total nitrogen in soils is in an unavailable organic form.[36] Organic nitrogen in the soil may be converted by microbial activity to ammonium ion, by the process called "ammonification". The ammonium ions thus produced can be held in the soil by negatively charged particles of clay and soil organic matter, and are therefore resistant to percolation. The ammonification process is dependent on soil temperature, aeration, and soil pH among other variables.

"Nitrification" is the process of microbial oxidation of the ammonium ion to the nitrate form. This occurs most rapidly under well aerated conditions, with a temperature of 60-85° F and a pH of 6.5 to 7.5.[36]

Nitrate is available for plant uptake but is also subject to leaching, the rate depending on soil conditions and properties. Under poor aeration, nitrate can be reduced by microbes to gaseous nitrogen and lost to the atmosphere through the process known as "denitrification". This occurs when oxidizable organic material is present to act as a source of electrons for nitrate reduction. Denitrification is more likely to occur in warm soils which have a neutral to alkaline pH.[36]

Ammonium ions, amino acids, and nitrate ions (via ammonia) may be incorporated into the protoplasm of microorganisms. At the death of the organisms, the organic nitrogen of the protoplasm may again be converted to available ammonium ions by the process of ammonification.

Most of the available information concerning reactions of nitrogen, particularly the microbial processes of the nitrogen cycle, as well as nitrogen transport data, has been developed in agriculturally-related research pertaining to the topmost, or soil, layer of the earth's crust. Those regions lying below the soil zone, including both the unsaturated zone above the water table and saturated ground-water zones, have received much less investigation in this regard. Information regarding nitrogen movement and reactions in the soil zone is important, however, because the fate of nitrogen in this zone undoubtedly plays a major role in determining the extent and nature of pollution of ground water by nitrogenous compounds and also because the processes occurring in this zone provide a basis for predicting probable movement and fate of nitrogen in the deeper zones of the earth's crust and for determining research needs pertaining to nitrogen in these zones. The remainder of this section considers in more detail available information concerning the movement and reactions of nitrogen compounds in the subsurface, principally the soil zone.

MOVEMENT OF GASES

Gases move through soil in response to pressure differentials within

the soil porespace. Physical processes affecting pressure differentials can result from unequal partial pressures of gases making up the soil atmosphere, differences in atmospheric pressures, temperature gradients in the soil profile, or displacement of the gas in the soil porespace by a liquid. Molecular diffusion of gases causes movement through the profile, depending on such rate-controlling factors as concentration gradients, gas temperature, molecular structure, and chemical reactivity of the gas.

Physical processes can be activated by biological processes occurring in the soil. Decomposers can create gas pressure or concentration differentials leading to a gas flow through the porespace, and adsorption of soil water by plant roots induces airflow into the soil to fill vacated porespaces.

Production of volatile gases, especially nitrous oxide and nitrogen, occurs when nitrate or nitrite is reduced in biochemical reactions favored by wet soil conditions, manure, and other organic material. Such denitrification reactions are inhibited by oxygen, and they rarely occur in dry, well-aerated soils. Ammonia can also be volatilized from the soil.

A constant emission of gases from the soil is improbable since the conditions favoring nitrogenous gas formation are episodic; however, the amounts that are emitted may constitute a considerable loss from the soil. Researchers confront problems in the lack of methodology and equipment needed to adequately identify and quantify the nitrogenous gases present in soil. A state of the art review of the techniques used is given by McGarity and Rajaratnam.[82] Continued work on the movement of nitrogenous gases is necessary to determine the importance of this factor in the nitrogen balance of the subsurface zone.

MOVEMENT OF NON-GASEOUS NITROGEN COMPOUNDS

The movement of water through the soil profile is of major significance to the nitrogen cycle in the subsurface environment. Displacement of gas in the soil by infiltrating water initiates gas movement and water in the porespace can produce anoxic conditions suitable for denitrification by facultative and anaerobic bacteria. It also produces habitat conditions favorable to many organisms because dissolved organic and inorganic nutrient material is transported by soil water as it moves in response to complex gradients caused by variations in pressure and capillarity.

The quantity of nitrogen leached from the soil is a function of many factors operating in the soil profile. These vary greatly with time, and their effects on each other complicate any quantitative evaluations of the rate and amount of nitrogen transfer caused by each. At the present time, information regarding these factors is qualitative in nature, but useful in understanding the process or in comparing the leaching potentials of different situations. Some variables affecting

the rate and amount of nitrogen leached from soils include:

1. Soil characteristics (texture, porosity, structure, consistency, soil moisture, depth of profile, percolation rates, etc.)

2. Climate characteristics (amount, frequency, duration and time of precipitation, rates of evapotranspiration, and temperature regimen)

3. Biological characteristics (presence or absence of plant cover, depth of root zone, nitrogen use characteristics of the vegetation, periods of plant growth, levels of soil organic matter, microbial and animal populations)

4. Cultural characteristics (land use patterns and soil management practices)

5. Nitrogen characteristics (amount and type of fertilizer application, type of fertilizer applied, amount of organic matter in the soil)

Interactions of these variables produce a complex, everchanging pattern of nitrogen distribution in soil profiles. Any nitrogen compound in the soil can be leached if the proper conditions are satisfied, but primary concern has been directed to the highly soluble inorganic forms. Ammonium ions can be leached once the cation exchange capacity of the soil is satisfied. During saturation periods, when oxygen levels are low and biological activities are reduced, physical adsorption may occur. The amount of adsorption decreases with increased concentrations of potassium cations. Where high concentrations of other cations exist, especially several hundred milligrams per liter of calcium and magnesium, they probably interfere with ammonium adsorption.[5]

The conversion of nitrogen compounds to anionic forms (nitrite and nitrate) promotes leaching, since most of the mineral fractions of soils are anionic. Determinants of movement of these compounds include the amount of water infiltrating the soil, soil moisture content at the beginning of the precipitation event, and the porosity and permeability of the soil. Nitrate leaching increases during wet periods, as soil moisture levels are high and evapotranspiration rates are reduced. Denitrification may occur during the leaching process, as indicated in studies of nitrate concentration beneath an irrigated field.[83]

Leaching of nitrate occurs during or shortly after precipitation events. The wetting front proceeds through the profile and satisfies the storage capacity of each successive zone. If the front is dissipated before passing through the root zone, no nitrates are removed. The evapotranspiration process causes capillary movement toward the soil surface. Nitrate salts carried in the water may enter the root hairs

of plants, or they may be deposited as salts in the surface soil as the water evaporates. During the next precipitation event, the nitrate salts dissolve and may be assimilated by plants or carried downward toward the water table.

In periods of active plant growth, evapotranspiration rates are high, plants have a high demand for nitrates and ammonia, and little leaching occurs. With cooler autumn weather in the temperate regions, nitrogen begins to accumulate in the profile. Winter and early spring precipitation may then leach the accumulated nitrogen to the ground water.

Nitrates leach more slowly from a profile containing a high percentage of clay or colloidal material than from a loamy sand. Water is held more readily by clay soils, and the dissolved nitrate is held with it. Ground-water contamination from increased nitrate concentration is much greater under light, sandy soils because of more rapid movement of the soil solution through the porous structure.

Organic nitrogen compounds per se are not usually considered a pollution threat to ground water. Mineralization of these compounds is of concern, however, since organic forms are generally converted to inorganic forms before much distance has been traveled from the originating source. Where water tables are high and respond quickly to surface water levels, as in swamps and marshes, the potential for leaching organic nitrogen along with inorganic forms increases.

NITRIFICATION

The process of nitrogen fixation results in the production of the ammonium ion, a cation which leaches fairly slowly. Classically, nitrification is a process performed by microbes capable of oxidizing reduced forms of nitrogen: ammonium is oxidized to nitrite, which in turn is oxidized to nitrate. Nitrate, a form of nitrogen readily usable by most plants, is anionic, leaches much more readily than does ammonium, and is subject ultimately to conversion to atmospheric nitrogen or nitrous oxide by denitrifiers.

Typical nitrifiers are autotrophic aerobic bacteria: Nitrosomonas is a common ammonium oxidizer, and Nitrobacter is a common nitrite oxidizer. While the process is related to the energy relations within these cells and is therefore essential to their metabolism, several heterotrophic organisms can also oxidize ammonium under appropriate conditions. These heterotrophs, which include bacteria, actinomycetes and fungi, can achieve large populations in soils. They are also capable of good growth under conditions unfavorable to nitrification, so apparently the process neither serves the same function nor follows the same metabolic pathway in all these organisms.[84] However, the most significant nitrification appears to be accomplished by the autotrophs.

Nitrifying populations are sensitive to a variety of environmental conditions. The nitrification capacity of soil has been linked to such diverse parameters as ammonium content, pH, oxygen content, moisture, temperature, organic matter, carbon dioxide content, cation exchange capacity of the soil, depth, cropping practices, season of the year, and soil treatment.[84,85,86,87,88] The exact effect of these factors is being studied in several localities.

Of all these factors, temperature and moisture are probably the most important ones governing nitrate accumulation in the medium-textured, limed soils of the midwestern United States.[86] It appears that temperature affects the rate of nitrification but not the total amount of nitrate produced over a 5-week period within the range of 16-20° C.[87] The optimum temperature range for nitrifying bacteria has been reported as 30-35° C, with little nitrification occurring above 40° C.[84] Nitrification is also minimal at or below 0° C.[88] Maximum accumulation of nitrate occurs at lower moisture tension than field capacity, the water content of the moist soil layer after capillary movement of water has become negligible. Most soils reach field capacity within 2 days or less after a rain or irrigation. Far from saturation, field capacities range from about 5 percent in very sandy soil to about 45 percent of the dry weight in clays. Apparently, there is an abrupt reduction in nitrification as the soil becomes nearly saturated with moisture.[87] However, as with most microbiological processes, the optimum conditions for nitrifiers vary with the type and strain of organism.

Nitrification studies have been performed in soil columns using known concentrations of ammonium ion added to columns containing known microbial species, population sizes, and even distribution of microbes through the soil. Reaction rates for individual stages in the process can then be calculated. Mathematical analysis of the kinetics of such experiments are given by McLaren and Skujins.[89] Such studies are the best available approach currently used to approximate nitrification under field conditions, and they are useful in making predictions. However, they are not subject to the variable nature of ecosystems and the important interactions of mixed and fluctuating populations, hydrodynamics, diffusion, temperature and soil surfaces. More studies need to be carried out with single variables although this will oversimplify the picture.

In the first stage of the classical nitrification pathway, ammonium is oxidized to nitrite by organisms such as Nitrosomonas. In the second stage nitrate is oxidized to nitrate by organisms such as Nitrobacter. The organisms responsible for this oxidation are aerobes and grow best in well-aerated soils of lightly alkaline pH. The pH for nitrification rates appears to be slightly higher in soil than in solution cultures.[90] Ammonium oxidizers do not proliferate in even slightly acidic soils, but they seem to be less sensitive to changes of temperature, ammonium concentration and moisture content than are nitrite oxidizers. When conditions are not optimum for complete nitrification, nitrite will accumulate in some soils. In the United States, for example, nitrite

accumulates in southern soils at low temperatures, while in northern soils it accumulates at high temperatures.[85]

Several factors have been shown to favor nitrite or nitrate accumulation following their production by soil microbes. If large amounts of urea, anhydrous ammonia or ammonium salts are added to soils of high pH, or to soils whose pH rises as the result of urea hydrolysis, nitrite can build up significantly. Under these conditions it has been shown to persist for at least nine months.[84] Nitrite does not persist in acid soils. Nitrate is formed during the cold periods, when plant demands are low, and is more subject to leaching from the root zone in autumn than during the spring.

Using equations derived from kinetic studies of nitrate accumulations, one can estimate the nitrate accumulation that should occur in soils similar to the loess-derived silt loams common in the midwestern United States. Such estimates can be made for any temperature between 0° and 25° C, and at any moisture tension from 0.1-15 bars, if the ammonium concentration is not limiting and if conditions are favorable for nitrification.[86]

Anything that inhibits the rate of nitrification results in less conversion of cationic ammonium to anions, and therefore retards the activity of denitrifiers that depend on nitrate for their activity. Retardation of nitrification can be accomplished by the additions of pesticides, particularly 2-chloro-6-(trichloromethyl) pyridine, by steam, or by chemical fumigants such as technical dichloropropenes or a mixture of methyl bromide, chloropicrin and propargyl bromide.[91,92] Certain plants may also produce inhibitors which may be excreted through the roots.[84]

Products of nitrification are subject to a variety of further transformations in completing the nitrogen cycle. These include uptake by plants and microbes, which incorporate them into organic material, denitrification, and chemical fixation by soil organic matter. When organisms decompose, an appreciable amount of their organic nitrogen compounds are fairly resistant to biological breakdown, and they remain in stable humus material. Humus is colloidal in nature, and this may further decrease its biological reactivity.[93,94] Humic nitrogen compounds and their resistance to biological transformations are as yet poorly understood, but they are being studied in physical, chemical and biological investigations.[93,95,96]

DENITRIFICATION

A balancing aspect of the nitrogen cycle is, in effect, the reversal of the processes of nitrogen fixation and nitrification. Denitrification occurs in anaerobic conditions when performed by microbial agents, although in strictly chemical reactions, it may occur in an environment of air. In biological systems, nitrate and nitrite are reduced to volatile gases, especially nitrous oxide and nitrogen, in reactions that are favored by wet soil condition and the presence of organic material such as manure. The process is inhibited by oxygen, and it rarely occurs in dry, well-aerated soil.

Many denitrifiers are facultative anaerobes. Under anaerobic conditions, they carry on anaerobic respiration, substituting nitrate or a related nitrogenous compound for oxygen as the terminal electron acceptor. The nitrate is thus reduced. The pathway usually described reduces nitrate to nitrite to nitrous oxide to nitrogen gas, although some intermediates (such as HNO, H_2N_2O or NO_2NH_2) have been postulated.

The strain of denitrifying organism determines which enzymes are present and what products will be formed. Several other factors determine the rate of the reactions. The pH of the soil environment is important, since denitrification is slow in acid but fast in alkaline media: it usually occurs in soils of pH 6 or above. The relative amounts of N_2O and N_2 produced are affected by temperature, with N_2O being predominantly formed at lower temperatures and N_2 at higher ones. Also, the ratio of ammonium to nitrate in the soil will affect the products formed: a one-to-one ratio of ammonium to nitrate favors the predominance of N_2O in the product, while a ratio of 0:1 results in the predominance of N_2.[81]

Conditions conducive to denitrification are commonly found in fine-textured, water-logged soils with high organic content. Water apparently has a direct effect on denitrification, as the closer the soil is to saturation, the more denitrification occurs there. Little occurs in soils less than about 60 percent saturated.[81] Because of this dependence on high water content, it is probable that denitrification may be quite extensive in the anaerobic capillary fringe zone just above water tables, where water is held in soil spaces by capillary action. This is especially indicated in and above saturated zones beneath agricultural areas that are fertilized with nitrates or irrigated with waters high in nitrate, since nitrate is readily leached from upper soil layers. In considering the fate of nutrients such as ammonia, urea and nitrate added to soils, it appears that 10-30 percent of the nitrogen added in fertilizer can be lost through denitrification alone.[97] High organic content is conducive to denitrification, since heterotrophic denitrifiers need oxidizable organic material as a source of carbon for synthesis of protoplasm and as a source of electrons for the reduction of nitrogenous compounds.

While it is commonly accepted that chemical denitrification also occurs in nature, there is considerable debate over its mechanisms and its extent. Chemical denitrification reactions are known to occur in normal aerobic soil. Nitrite ions can react with many compounds, including some ammonium salts, simple amines like urea, non-nitrogenous carbohydrates and sulfur compounds, to generate nitrogen gas under slightly acid conditions. These reactions probably occur when soil conditions are favorable for nitrification reactions, and for the growth of aerobic microbes and plants, rather than in the anaerobic, neutral to alkaline conditions that support biological denitrification. Nelson and Bremner report that nitrogen gas forms readily from reactions involving decomposition of nitrite in acidic soils high in organic matter.[98]

SECTION VI

SPECIFIC INCIDENTS OF NITROGEN CONTAMINATION IN GROUND WATER

The detection of nitrogen contamination in ground-water supplies is not new, as Abbott points out in one of his articles. Data obtained in the Iowa Water Survey made in 1935-36 showed that in 200 water samples analyzed, nitrate values varied from 0-125 mg/l in domestic and municipal wells. He also discusses a later survey in North Dakota which revealed that of 151 dug wells sampled in North Dakota, about one-half of them contained more than 10 mg/l of nitrate-nitrogen.[13]

The problem of ground-water contamination is not one which is unique to the United States. Holland, which takes about 77 percent of its water supply from underground sources, detected the presence of nitrate and nitrite ions in some of its municipal water supplies in a survey in 1960.[99] Subbotin also reports that well water around Leningrad, U. S. S. R., contains some nitrates equivalent to about 20-40 mg/l of nitrogen.[9]

Ballentine discusses a survey conducted in the state of Illinois in which 30 percent of the wells less than 25 feet in depth showed concentrations in excess of the 45 mg/l Public Health Service Drinking Water Standard recommendations.[100] Walker also reports that chemical analysis of ground-water samples from throughout Illinois indicated that nitrate pollution in aquifers was widespread, especially in rural parts of the state. In Washington, County, Illinois, recent analyses of water samples from 263 farm-supply wells showed a median nitrate concentration of 143 mg/l and more than the recommended 45 mg/l level was found in over 73 percent of the wells sampled.[101] Larson reports that in Livingston County, Illinois, 46 wells within a 12 to 13 square mile area were sampled and 26 of these samples showed nitrate concentrations greater than 15 mg/l. In another area representing about 25 to 30 square miles in Iroquois County, Illinois, only 3 of 201 samples showed nitrate concentrations greater than 15 mg/l. Two of these 3 samples showed nitrate values greater than 45 mg/l.[102]

In some counties in Missouri, more than 75 percent of the wells surveyed were contaminated by the nitrates. Some wells in close proximity to feedlot areas showed values of more than 300 mg/l nitrate-nitrogen.[29] In a more recent survey in the state of Missouri, including 45 counties and representing more than 5000 wells, about 45 per cent contained over 5 mg/l nitrate-nitrogen.[10]

A comprehensive study by the Minnesota Department of Health in the Minneapolis-St. Paul area consisted of collection of random samples from 63,000 wells which served more than 250,000 people.[103] About 46.5 percent of the samples showed evidence of nitrate-nitrogen contamination and 10.6 percent showed more than 10 mg/l nitrate-nitrogen.

Suffolk County, New York has been the topic of a number of well publicized investigations and the results of some surveys show the impact of suburban growth on ground-water quality. This county includes an area of about 922 square miles, with a population in 1960 of 665,000. About 59 percent of the population obtains water from 90 communal or public water supplies. In 1958 it became evident to the Suffolk County Health Department that the quality of the water from private wells was poor and deteriorating. Townships and municipal suppliers were asked to cooperate in programs leading to the extension of public water supplies to serve existing residential areas. The first group of these wells was constructed in August and September of 1958. In February and March of 1961, samples were collected from 47 of these wells. During this 2 1/2 year period of time, a number of the wells had become contaminated with nitrate ions and free ammonia. Of the 47 wells surveyed, 5 showed greater than 10 mg/l nitrate-nitrogen.[104]

In the same vicinity, Kings County, Long Island, New York, according to a recent United States Geological Survey study, leakage from sewers may be a principal source of the nitrate and total nitrogen in ground-water supplies.[75] Landfill leachate has been blamed for ammonia contamination of ground water in the same county. This is only one of about 100 cases of ground-water contamination problems in the northeastern states related to landfill sites.[75]

An investigation into the degree of contamination of ground-water supplies by nitrate-nitrogen in the central Wisconsin farm area of Marathon County revealed that 55 percent of the wells contained nitrate concentrations of 45 mg/l or more. Among 242 wells investigated, 82 private wells were sampled 2 times per month for a period of 14 months. Nearly 70 percent of the 82 wells contained nitrate levels of 45 mg/l or more throughout the period.[12] The variations in nitrate concentration were closely related to the amount of precipitation and concentration was highest during heavy rainy seasons and lowest during dry periods for the majority of wells examined.

Stewart and co-workers have investigated the ground water under irrigated fields and feedlots in the South Platte River Valley of Colorado. The average concentration of ammonia-nitrogen of the waters from beneath 28 irrigated fields was 0.2 mg/l and only 2 samples contained as much as 1 mg/l. Water from beneath 29 feedlots averaged 4.5 mg/l of nitrogen (as ammonia) and 15 of those contained more than 1 mg/l. Seven of these

samples were above 5 mg/l and the highest value was 38 mg/l.[17] Another case of interest in the state of Colorado is a Colorado city of 7,500 people where a shallow aquifer water supply had reached nitrate levels of over 60 mg/l (as nitrate) by 1962.[105]

Concern has also been shown in the state of Nebraska for possible contamination of ground water by nitrate and other nitrogen forms. Some reports of high nitrate water from several wells in northern Holt County caused the Lincoln, Nebraska office of the United States Geological Survey to look into the problem of nitrate contamination. Water samples were collected from 71 wells and nitrate concentrations ranged from 0.1 to 400 mg/l. The Delaware Geological Survey also reveals that 25 percent of the shallow wells in the state yield water with nitrate levels above 20 mg/l.[75]

Leakage of wastewater from surface impoundments has been investigated in 57 cases of ground-water contamination in the northeastern United States. Many of the samples examined in these investigations showed evidence of contamination by ammonia and nitrate-nitrogen.[72] Also, in the northeastern United States, 36 cases of ground-water contamination have apparently been caused by spills and surface discharge. Three of these showed evidence of contamination by nitrate-nitrogen. Shallow disposal wells in freshwater aquifers are used in this part of the country for disposal of a variety of liquid wastes including storm water, sewage, cooling water, and industrial effluent. Nitrates have been reported in some samples collected from wells in close proximity to these disposal sites.[22]

It would appear that many of the cases involving contamination could be attributed to man's activities, but natural contamination has been cited also. Runnels County and some other counties in this area of Texas show evidence of widespread nitrate contamination as indicated by a 1951 survey of approximately 20,000 wells showing nitrate-concentrations greater than 20 mg/l in approximately 3,000 wells and some concentrations as high as 1,000 mg/l. Large quantities of natural nitrate are present in the soil system of this area and the porosity of the soil is low. Changed climatic conditions have provided sufficient precipitation to raise the water table, thus resulting in the dissolution of part of the soil nitrate.[106]

Specific cases of ground-water contamination have been documented in a number of states as well as some foreign countries. These cases represent contamination due to natural causes and also those due to the activities of man. The contaminations cover a wide range of concentrations from low to very high nitrate-nitrogen values. The situation is one which should receive attention because the problem is widespread and can be expected to continue if proper plans for abatement are not implemented.

SECTION VII

REFERENCES

1. Engberg, R. A. The Nitrate Hazard in Well Water. Nebraska Water Survey Paper 21. 1967. p. 1-11.

2. Lenain, A. F. The Impact of Nitrates on Water Use. Journal of the American Water Works Association. 59:1050-1051, August, 1967.

3. Dunlap, W. J. and J. F. McNabb. Subsurface Biological Activity in Relation to Ground Water Pollution. Environmental Protection Agency, Ada, Oklahoma. Publication Number EPA-660/2-73-014. September, 1973. p. 4-5.

4. Miller, D. W., F. A. DeLuca, and T. L. Tessier. Ground Water Contamination in the Northeast States. Environmental Protection Agency, Washington, D. C. Publication Number EPA-660/2-74/056. June, 1974. p. 8-22.

5. Preul, H. C. and G. S. Schroepfer. Travel of Nitrogen in Soils. Journal Water Pollution Control Federation. 40:30-48, January, 1968.

6. Corey, J. C., D. Kirkham, and D. R. Nielsen. The Movement of Chloride and Nitrate through Certain Iowa Soils. Iowa Academy of Science. 74:131-141, 1967.

7. Christy, M., J. R. Brown, and L. S. Murphy. Nitrate in Soils and Plants Guide. Columbia, University of Missouri Extension Division, 1965. p. 9804-9806.

8. Winton, E. F., R. G. Tardiff, and L. J. McCabe. Nitrate in Drinking Water. Journal of the American Water Works Association. 63:93-98, 1971.

9. Subbotin, F. N. Nitrates in Drinking Water and Their Effect on the Formation of Methemoglobin. S. M. Kirov Order of Lenin Army Medical Academy (USSR). 25(2):63-67, 1961.

10. Smith, G. E. Nitrate Problems in Plants and Water Supplies in Missouri. (Presented at Second Annual Symposium on the Relation of Geology and Trace Elements to Nutrition, 92nd Annual Meeting of the American Public Health Association. New York City. October 7, 1964.) 21 p.

11. Keller, W. D. and G. E. Smith. Ground-Water Contamination by Dissolved Nitrate. The Geological Society of America. Special Paper 90. 1967. p. 47-56.

12. Crabtree, K. T. Nitrate and Nitrite Variation in Ground Water. Department of Natural Resources, Madison, Wisconsin. Technical Bulletin No. 58. 1972. p. 2-22.

13. Abbott, G. A. High Nitrates in Drinking Waters and Their Toxicity to Infants. In: Annual Proceedings, North Dakota Academy of Science. 1949. p. 51-54.

14. Case, A. A. Some Aspects of Nitrate Intoxication in Livestock. Journal of the American Veterinary Medical Association. 130(8): 323-328, 1957.

15. Grundman, J. E. Nitrates Danger for Humans, Too. Missouri Ruralist. p. 24-25. February 27, 1965.

16. National Research Council. Accumulation of Nitrate. Washington, D. C., National Academy of Sciences, 1972. p. 5-23.

17. Stewart, B. A., F. G. Viets, Jr., G. L. Hutchinson, and W. D. Kemper. Nitrate and other Water Pollutants under Fields and Feedlots. Environmental Science and Technology. 1:736-739, September, 1967.

18. Coffee, R. C. and W. F. Bartholomew. Some Aspects of Ammonia Sorption by Soil Surfaces. Soil Science Society of America Proceedings. 28(4):485-490, July-August, 1964.

19. Schmidt, K. D. Nitrate in Ground Water of the Fresno-Clovis Metropolitan Area, California. Ground Water. 10(1)50:61, January-February, 1972.

20. Delwiche, C. C. The Nitrogen Cycle. Scientific American. 223(3): 69, September, 1970.

21. DeRossi, G. LaFisszione del Azote Atmospherico el Terreno. Annali Della Facolta di Agraria (Milan). 3:140-175, 1945.

22. Ingham, G. J. Effect of Minerals Absorbed from the Atmosphere in Maintaining Soil Fertility. Soil Science. 70:205-212, 1950.

23. Malo, B. A. and E. R. Purvis. Soil Absorption of Atmospheric Ammonia. Soil Science. 97:242-274, April, 1964.

24. Hanawalt, R. B. Environmental Factors Influencing the Sorption of Atmospheric Ammonia by Soils. Soil Science Society of America Proceedings. 33(2):231-234, March-April, 1969.

25. Smith, G. E. Why Nitrates in Water Supplies. Hoard's Dairyman. 110(18):1048-1049, September 25, 1965.

26. Bremner, J. M. Organic Nitrogen in Soils. In: Soil Nitrogen, Agronomy Monograph 10, Bartholomew, M. V. (ed.). Madison, American Society of Agronomy, 1965. p. 93-149.

27. Goldberg, M. C. Sources of Nitrogen in Water Supplies. In: Agricultural Practices and Water Quality. Ames, Iowa University Press, 1970. p. 94-124.

28. Riley, T. M. Our Mineral Resources. New York, John Wiley & Sons, Inc. 1959. 338 p.

29. Smith, G. E. Nitrate Pollution of Water Supplies. In: Trace Substances Environmental Health-3, Proceedings of University of Missouri's 3rd Annual Conference, 1970. p. 273-287.

30. Hutchinson, G. E. Nitrogen Bio-Geo-Chemistry of the Atmosphere. Bio-chemistry American Scientist. 32:178-195, 1944.

31. Olsen, R. J., R. F. Hensler, O. J. Attoe, J. Osborne, and S. A. Witzel, Comparison of Inorganic Nitrogen Contents of Undisturbed, Cultivated, and Barnyard Soil Profiles in Wisconsin. Soil Science Society of America Proceedings. 34(4):699-701, July-August, 1970,

32. Allen, S. E., A. Carlisle, E. J. White and C. C. Evans. Plant Nutrient Content of Rainwater. Journal of Ecology. 56(2):497-504, 1968.

33. Herman, F. A. and E. Gorham. Total Mineral Activity Acidity, Sulfur, and Nitrogen in Rain and Snow at Kentville, Nova Scotia. Tellus (Sweden). 9:180-183, 1957.

34. Erikson, E. Composition of Atmospheric Precipitation: 1. Nitrogen Compounds. Tellus(Sweden). 4:215-232, 1952.

35. Angstrom, A. and L. Hogberg. The Content of Nitrogen (Ammoniacal Nitrogen and Nitrite Nitrogen) in Atmospheric Precipitation. Tellus(Sweden). 4:31-42, 1952.

36. Keeney, D. R. and L. W. Walsh. Available Nitrogen in Rural Ecosystems: Sources and Fate. Hortscience. 7(3):219-223, June, 1972.

37. Luebs, R. A., K. R. Davis, and A. E. Lang. Enrichment of the Atmosphere with Nitrogen Compounds Volatilized from a Large Dairy Area. Journal of Environmental Quality 2(1):137-141, January-March, 1973.

38. Dawes, J. H., T. E. Larson, and R. H. Harmeson. Nitrate Pollution of Water. In: Frontiers in Conservation. Proceedings of the 24th Annual Meeting of the Soil Conservation Society of America, August, 1969. Fort Collins, Colorado State University, 1970. p. 94-102.

39. Keeney, D. R. and L. W. Walsh. Available Nitrogen in Rural Ecosystems: Sources and Fate. Hortscience. 7(3):492, June, 1972.

40. Stevenson, F. J. Origin and Distribution of Nitrogen in Soil. In: Soil Nitrogen, Agronomy Monograph 10, Bartholomew, W. V. (ed.). Madison, American Society of Agronomy, 1965. p. 1-42.

41. Stefanson, R. C. Evolution Patterns of Nitrous Oxide and Nitrogen in Sealed Soil-Plant Systems. Soil Biology and Biochemistry. 5: 167-170, January, 1973.

42. Brezonik, P. L. Nitrogen Sources and Cycling in Natural Waters. Environmental Protection Agency, Gainesville, Florida. Publication Number EPA-660-3-73-002. 1973.

43. Hutchinson, G. L. and F. G. Viets, Jr. Nitrogen Enrichment of Surface Water by Absorption of Ammonia Volatilized from Cattle Feedlots. Science. 166(3904):514-515, October, 1969.

44. Lipper, R. I., J. R. Miner, and G. H. Larson. Cattle Feedlot Waste Problems. (Presented at Oklahoma Cattle Feeders Seminar. Stillwater. February 2-3, 1967.) 9 p.

45. Viets, F. G. and R. H. Hazeman. Factors Affecting the Accumulation of Nitrate in Soil, Water, and Plants. Agriculture Handbook Number 413. United States Department of Agriculture. November, 1971. 63 p.

46. Gillham, R. W. and L. R. Webber. Nitrogen Contamination of Groundwater by Barnyard Leachates. Journal Water Pollution Control Federation. 41:1752-1762, October, 1969.

47. Butchbaker, A. F., J. E. Ganton, G. W. A. Mahoney, and M. D. Paine. Evaluation of Beef Cattle Feedlot Waste Management Alternatives. Environmental Protection Agency, Stillwater, Oklahoma. Publication Number EPA-13040 FX611071. November, 1971. 322 p.

48. Mielke, L. N., J. R. Ellis, N. F. Swanson, J. C. Lorimor, and T. M. McCalla. Ground Water Quality in Fluctuation in a Shallow Unconfined Aquifer Under a Level Feedlot. In: Relationship of Agriculture to Soil and Water Pollution, Proceedings of Cornell University Conference on Agricultural Waste Management. 1970. p. 31-40.

49. McCalla, T. M. Beef Cattle Feedlot Waste Management Research in the Great Plains. (Presented at Control of Agriculture-related Pollution in the Great Plains, Seminar. Lincoln, Nebraska. July 24-25, 1972.)

50. Lorimor, J. C., L. N. Mielke, L. F. Elliott, and J. R. Ellis. Nitrate Concentrations in Groundwater Beneath a Beef Cattle Feedlot. Water Resources Bulletin. 8(5):999-1005, October, 1972.

51. Miner, J. R. and T. L. Willrich. Livestock Operations and Field Spread Manure as Sources of Pollutants. Agricultural Practices and Water Quality. Ames, Iowa State University Press, 1970. p. 231-240.

52. Stewart, B. A., F. G. Viets, Jr., G. L. Hutchinson, W. D. Kemper, and F. E. Clark. Distribution of Nitrates and other Water Pollutants under Fields and Corrals in the Middle South Platte Valley of Colorado. Agricultural Research Service. Publication Number ARS 41-134. December, 1967. 206 p.

53. Battelle Memorial Institute. Inorganic Fertilizer and Phosphate Mining Industries - Water Pollution and Control. Environmental Protection Agency. Publication Number 12020 FPD 09/71. September, 1971.

54. Nelson, L. B. Agricultural Chemicals in Relation to Environmental Quality: Chemical Fertilizers, Present and Future. Journal of Environmental Quality. 1(1):2-6, January-March, 1972.

55. Farrell, J. B. Nitrogen in Industry. (Presented at Symposium on Nitrogen in Soil and Water. Hespeler, Ontario. March 30-31, 1971.)

56. Commoner, B., G. Shearer, and D. Kohl. Origins of Nitrates in Surface Water, First Year Progress Report for a Study of Certain Ecological, Public Health, and Economic Consequences of the Use of Inorganic Nitrogen Fertilizer. Center for the Biology of Natural Systems, Washington University, St. Louis, Missouri. May 5, 1972.

57. Walker, W. H. Ground Water Nitrate Pollution in Rural Areas. Ground Water. 11(5):19-22, September-October, 1973.

58. Walker, W. H., T. R. Peck, and W. D. Lembke. Farm Ground Water Nitrate Pollution--A Case Study. (Presented at American Society of Chemical Engineers Annual and National Environmental Engineering Meeting. Houston, Texas. October 16-22, 1972.) 25 p.

59. Nightingale, H. I. Nitrates in Soil and Ground Water Beneath Irrigated and Fertilized Crops. Soil Science. 114(4):300, October, 1972.

60. Feth, J. H. Nitrogen Compounds in Natural Waters--A Review. Water Resources Research. 2(1):41-58, January-February, 1966.

61. Johnston, W. R., F. Ittihadieh, R. M. Daum, and A. F. Pillsbury. Nitrogen and Phosphorus in Tile Drainage Effluent. Soil Science Society of America Proceedings. 29(3):287-289, 1965.

62. Fitzsimmons, D. W., G. C. Lewis, D. V. Naylor, and J. Busch. Nitrogen, Phosphorus and other Inorganic Materials in Waters in a Gravity Irrigated Area. Transactions of the American Society of Agricultural Engineers. 15(2):292-295, March-April, 1972.

63. Bower, C. A., and L. V. Wilcox. Nitrate Content of the Upper Rio Grande as Influenced by Nitrogen Fertilization of Adjacent Irrigated Lands. Soil Science Society of America Proceedings. 33(6):971-973, November-December, 1969.

64. Moe, P. G., J. V. Mannering, and C. B. Johnson. Loss of Fertilizer Nitrogen in Surface Runoff Water. Soil Science. 104(6):389-394, December, 1967.

65. Aldrich, S. R. The Influence of Cropping Patterns, Soil Management, and Fertilizer on Nitrates. (Presented at Proceedings of the 12th Sanitary Engineering Conference on Nitrate and Water Supply, Source and Control. February 11-12, 1970.)

66. Pratt, P. F. Nitrate in the Unsaturated Zone under Agricultural Lands. Environmental Protection Agency. Publication Number EPA 16060 DOE04/72. April, 1972. 45 p.

67. Shaw, E. C. and P. Wiley. Nitrate Ion Concentration in Well Water. California Agriculture. 23:11, May, 1969.

68. Reinhorn, T. and Y. Avinmelech. Nitrogen Release Associated with the Decrease in Soil Organic Matter in Newly Cultivated Soils. Journal of Environmental Quality. 3(2):118-121, April-June, 1974.

69. Carter, D. L, J. A. Bondurant, and C. W. Robbins. Water-Soluble NO_3- Nitrogen, PO_4-Phosphorus, and Total Salt Balances on a Large Irrigation Tract. Soil Science Society of America Proceedings, 35(2):331-335, March-April, 1971.

70. Kilmer, V. J. and J. C. Barber, Fertilizer Use and Misuse. (Presented at Symposium on Nitrogen in Soil and Water, Hespeler, Ontario. 1971.)

71. Smith, G. E. Fertilizer Nutrients as Contaminants in Water Supplies. (Presented at American Association for the Advancement of Science Meeting, Washington, D. C., December 27, 1966.)

72. Miller, D. W., F. A. DeLuca, and T. L. Tessier. Ground Water Contamination in the Northeast States. Environmental Protection Agency. Washington, D. C. Publication Number EPA-660/2-74-056. June, 1974. p. 219-272.

73. National Research Council. Accumulation of Nitrate. Washington, D. C., National Academy of Sciences, 1972. p. 106.

74. Hanson, A. M. and G. F. Lee. Forms of Inorganic Nitrogen in Domestic Wastewater. Journal Water Pollution Control Federation. 43:2271-2279, November, 1971.

75. Miller, D. W., F. A. DeLuca, and T. L. Tessier. Ground Water Contamination in the Northeast States. Environmental Protection Agency, Washington, D. C. Publication Number EPA-660/2-74-056. June, 1974. p. 171.

76. Walker, W. H., T. R. Peck, and W. D. Lembke. Farm Ground Water Nitrate Pollution--A Case Study. (Presented at American Society of Chemical Engineers Annual and National Environmental Engineering Meeting. Houston, Texas. October 16-22, 1972.) p. 1516.

77. Boyle, W. C. and R. K. Ham. Biological Treatability of Landfill Leachate. Journal Water Pollution Control Federation. 46:806-872, May, 1974.

78. Miller, D. W., F. A. DeLuca, and T. L. Tessier. Ground Water Contamination in the Northeast States. Environmental Protection Agency, Washington, D. C. Publication Number EPA-660/2-74-056. June, 1974. p. 22-25.

79. Schmidt, D. L. Soil Nitrification and Nitrates in Waters. Public Health Reports. 71(5):497-503, 1956.

80. Christensen, M. H. and P. Harremöes. Biological Denitrification in Water Treatment. Department of Sanitary Engineering. Technical University of Denmark. Report 2-72. 1972.

81. Broadbent, F. E. and F. Clark. Denitrification. In: Soil Nitrogen, Agronomy Monograph 10, Bartholomew, W. V. (ed.). Madison, American Society of Agronomy, 1965. p. 347-362.

82. McGarity, A. W. and J. A. Rajartnam. Apparatus for the Measurement of Losses of Nitrogen as Gas from the Field and Simulated Field Environments. Soil Biology and Biochemistry. 5(1):131-132, January, 1973.

83. Meek, D. D., L. B. Grass, and A. J. Mackenzie. Applied Nitrogen Losses in Relation to Oxygen Status in Soils. Soil Science Society of America Proceedings. 33(4):575-578, July-August, 1969.

84. Alexander, M. Nitrification. In: Soil Nitrogen, Agronomy Monograph 10, Bartholomew, W. V. (ed.). Madison, American Society of Agronomy, 1965. p. 309-346.

85. Mahendrappa, M. D., R. L. SMith, and A. T. Christiansen. Nitrifying Organisms Affected by Climatic Region in Western United States. Soil Science Society of America Proceedings. 30(1):60-62, January-February, 1966.

86. Sabey, B. R. Influence of Soil Moisture Tension on Nitrate Accumulation in Soils. Soil Science Society of America Proceedings. 33(2):263-266, March-April, 1969.

87. Parker, D. T. and W. E. Larson. Nitrification as Affected by Temperature and Moisture Content of Mulched Soils. Soil Science Society of America Proceedings. 26(3):238-242, May-June, 1962.

88. Campbell, C. A., W. A. Ferguson, and F. G. Warder. Winter Changes in Soil Nitrate and Exchangeable Ammonium. Canadian Journal of Soil Science. 50:151-162, 1970.

89. McLaren, A. D. and J. Skujins. Trends in the Biochemistry of Terrestrial Soils. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 1-15.

90. Marshall, K. C. Sorptive Interactions Between Soil Particles and Microorganisms. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 409-442.

91. Alexander, M. Microorganisms and Chemical Pollution. Bioscience. 23(9):509-515, 1973.

92. Good, J. M. and R. L. Carter, Nitrification Lag Following Soil Fumigation. Phytopathology. 55(10):1147-1150, 1965.

93. Van Dijk, H. Colloid Chemical Properties of Humic Matter. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 16-33.

94. Jansson, S. L. Use of ^{15}N in Studies of Soil Nitrogen. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 129-162.

95. Felbeck, G. T., Jr. Chemical and Biological Characterization of Humic Matter. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 36-57.

96. Schnitzer, M. Characterization of Humic Constitutents by Spectroscopy. In: Soil Biochemistry, Vol. 2, McLaren, A. D. and J. Skujins (ed.). New York, Marcel Dekker, Inc., 1971. p. 60-93.

97. Kurtz, L. T. The Fate of Applied Nutrients on Soils. Journal of Agricultural and Food Chemistry. 18(5):773-780, 1970.

98. Nelson, D. W. and J. M. Bremner. Gaseous Products of Nitrite Decomposition in Soils. Soil Biology and Biochemistry. 2(3):203-215, 1970.

99. Baars, J. K. Experiences in the Netherlands with Contamination of Ground Water. In: Groundwater Contamination, Proceedings of 1961 Symposium held in Cincinnati, Ohio, April 5-7, 1961. Cincinnati, U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Technical Report W61-5, 1961, p. 56-63.

100. Ballentine, R. K., S. R. Reznik, and C. W. Hall. Subsurface Pollution Problems in the United States. Environmental Protection Agency, Washington, D. C. Report TS-00-72-02. May, 1972. p. 14-15.

101. Walker, W. H. Ground Water Nitrate Pollution in Rural Areas. Ground Water. 11(5):111-112, September-October, 1973.

102. Larson, T. E. Occurrence of Nitrate in Well Waters. University of Illinois Water Resource Center, Urbana, Project 65-05G. June, 1966. p. 5-6.

103. Woodward, F. L. Ground Water Contamination in the Minneapolis and St. Paul Suburbs. In: Groundwater Contamination, Proceedings of 1961 Symposium held at Cincinnati, Ohio, April 5-7, 1961. Cincinnati, U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Technical Report W61-5, 1961. p. 56-63.

104. Flynn, J. M. Impact of Suburban Growth of Ground Water Quality in Suffolk County, New York. In: Groundwater Contamination, Proceedings of 1961 Symposium held in Cincinnati, Ohio, April 5-7, 1961. Cincinnati, U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Technical Report W61-5, 1961. p. 56-63.

105. Winton, E. F. The Health Effects of Nitrates in Water. In: Proceedings 12th Sanitary Engineering Conference on Nitrate and Water Supply: Source and Control, University of Illinois, February 11-12, 1970. Urbana, Illinois University, College of Engineering, 1970. p. 55.

106. Jones, D. C. An Investigation of the Nitrate Problem in Runnels County, Texas. Environmental Protection Agency, Washington, D. C. Publication Number EPA-R2-73-267. June, 1973. p. 1-8.